

NASA FILE COPY

Loan expires on last  
date stamped on back cover.

PLEASE RETURN TO  
REPORT DISTRIBUTION SECTION  
LANGLEY RESEARCH CENTER  
NATIONAL AERONAUTICS AND  
SPACE ADMINISTRATION  
Langley Field, Virginia



N82975 X

CASE FILE  
COPY

[Reprinted from the Journal of The American Ceramic Society, Vol. 44, No. 2. February, 1961.]

# Spontaneous Cracking in Unfired Magnesia Compacts Upon Standing in Air

by MYRON O. DAVIES, HUBERT H. GRIMES, and CHARLES E. MAY

Lewis Research Center, National Aeronautics and Space Administration, Cleveland, Ohio

Analytical-grade magnesium oxide powder without binder was compressed hydrostatically to 50,000 lb. per sq. in. to form compacts. When exposed to moist air immediately after pressing, these compacts developed irregularly shaped cracks. Controlled tests, in which these compacts were exposed for various lengths of time to various atmospheres, indicated that in general water vapor, carbon dioxide, and residual stresses had to be present if cracking was to occur. The probable cause of the cracking was the formation of a less dense and mechanically weak basic carbonate of magnesium at crystallite surface points of high stress concentration which developed during the compacting. The adsorption of dry  $\text{CO}_2$  at such sites prevented subsequent delayed fracture.

## I. Introduction

**S**PONTANEOUS cracking, often referred to as delayed fracture, may be regarded as a special case of stress rupture of materials in which the interaction with the surrounding fluid has a significant effect on the time to rupture. In one type of delayed fracture, external stresses are applied to the specimens. Several examples of this type reported in the literature are the fracture of stressed specimens of glass in an environment of air,<sup>1</sup> sintered alumina in air,<sup>2</sup> brass in ammonia,<sup>1(a)</sup> and polymethyl methacrylate in liquid carbon tetrachloride.<sup>1(a)</sup> Less commonly encountered is a second

type of delayed fracture in which no external stresses are applied; the only stresses involved are the residual stresses introduced during forming operations. A possible example of this type is the fragmentation of the intermetallic compound  $\text{Mg}_2\text{Sn}$  in water.<sup>3</sup> Single crystals of this compound crack when placed in distilled water and continue to subdivide when allowed to remain in contact with the water. A more commonplace example of delayed fracture of this type is the cracking of commercial basic firebrick. These brick, composed largely of  $\text{MgO}$ , have been observed to disintegrate spontaneously in moist air<sup>4</sup> unless they have been pretreated with certain gases or solutions to prevent atmospheric attack.<sup>5</sup>

Several cases of this type of delayed fracture (uranium carbide, thorium carbide, and magnesium oxide in air) have been observed at this laboratory, the most recent being the spontaneous cracking of compacted unfired pure magnesium oxide. Compacts of analytically pure  $\text{MgO}$  powder prepared

62 [356B] 469-76 (1949); *Ceram. Abstr.*, 1949, November, p. 254f.

(c) T. C. Baker and F. W. Preston, "Fatigue of Glass under Static Loads," *J. Appl. Phys.*, 17 [3] 170-78 (1946); *Ceram. Abstr.*, 1946, August, p. 149.

(d) T. C. Baker and F. W. Preston, "Effect of Water on Strength of Glass," *J. Appl. Phys.*, 17 [3] 179-88 (1946); *Ceram. Abstr.*, 1946, August, p. 137.

(e) J. L. Glathart and F. W. Preston, "Fatigue Modulus of Glass," *J. Appl. Phys.*, 17 [3] 189-95 (1946); *Ceram. Abstr.*, 1946, August, p. 137.

<sup>2</sup> (a) S. Pearson, "Delayed Fracture of Sintered Alumina," *Proc. Phys. Soc. (London)*, 69 [444B] 1293-96 (1956); *Ceram. Abstr.*, 1957, July, p. 171d.

(b) L. S. Williams, "Stress Endurance of Sintered Alumina," *Trans. Brit. Ceram. Soc.*, 55 [5] 287-312 (1956); *Ceram. Abstr.*, 1957, January, p. 28d.

<sup>3</sup> W. D. Robertson and H. H. Uhlig, "Observation of Corrosion Cracking Without Stress," *J. Appl. Phys.*, 19 [9] 864-65 (1948).

<sup>4</sup> H. Schreiner, "Die Hydratbildung bei Sintermagnesiten" (Formation of Hydrate in Sintered Magnesites), *Radex Rundschau*, 1952, No. 6, pp. 255-60; *Ceram. Abstr.*, 1953, August, p. 141i.

<sup>5</sup> P. Lanser and N. Skalla, "Hydratationsbeständige Magnesitsteine" (Hydration-Resistance Magnesite Refractories), *Radex Rundschau*, 1953, No. 6, pp. 40-43.

Received May 9, 1960; revised copy received August 11, 1960.

Myron O. Davies and Hubert H. Grimes are members of the Solid State Physics group and Charles E. May is head of the High Temperature Chemistry Section, Lewis Research Center, National Aeronautics and Space Administration.

<sup>1</sup> (a) C. Gurney and Z. Borysowski, "Delayed Fracture of Materials under Tension, Torsion, and Compression," *Proc. Phys. Soc. (London)*, 61 [347] 446-52 (1948); *Ceram. Abstr.*, 1949, November, p. 254d.

(b) C. Gurney and S. Pearson, "Effect of Surrounding Atmosphere on Delayed Fracture of Glass," *Proc. Phys. Soc. (London)*,





Fig. 1. Appearance of cracked magnesium oxide compact.

for another research program were found to develop irregularly shaped hairline cracks (as shown in Fig. 1) when exposed to air for several hours subsequent to the hydrostatic pressing. The experiments reported in this paper were carried out to determine the reason for this cracking and possible ways to prevent it. Since the cracking was believed to be caused by components of the air, the experimental program involved exposing compacted specimens to controlled atmospheric environments and determining the chemical reactions involved in the cracking procedure as well as their kinetics. The influence of the annealing process and compacting pressure was also noted.

## II. Experimental Procedure

The general procedure adopted in these experiments consisted of forming compacts of pure MgO powder identical to the specimens which had fragmented after an exposure of several hours to air. The specimens were formed by placing 8 gm. of analytical-grade MgO (described in Table I) without a binder into a double covering of thin rubber tubing  $\frac{5}{8}$  and  $\frac{3}{4}$  in. in diameter and slowly pressing to 50,000 lb. per sq. in. (in approximately 3 minutes). The pressure was slowly released (in approximately 3 minutes), the rubber bags were opened, and the compacts were removed to the experimental environments. (The bulk density of such compacts was 2.0 gm. per cm.<sup>3</sup>.) The environments used were wet and dry air, vacuum, air at 110°C., argon at 1250°C., wet and dry CO<sub>2</sub>, and water vapor. In some experiments the compacts were placed in small sealed bottles containing only a limited amount of gas, whereas in other experiments unlimited amounts of gas were available. In general, each experiment was terminated with the appearance of cracks, but, in certain instances where no cracking occurred, the specimens were moved to a second environment. In other experiments successive 250-ml. portions of air were introduced into a flask containing the specimen, and the number of fillings needed to produce cracking was counted. Each portion of air was allowed to remain in contact with the specimens for fixed lengths of time, the flask was evacuated, and a new portion was then introduced into the flask. Quantitative determinations of the amounts of adsorbed or reacted gas were obtained by chemical analyses and weight increases of certain specimens; the rate of weight gain was also determined on certain specimens. The details of the individual conditions of the experiments are presented in Tables II and III along with the results of these tests.

Although several hydrostatic pressures were tried in the preparation of specimens (from 2000 to 50,000 lb. per sq. in.), only those pressed at 50,000 lb. per sq. in. were examined in detail.

Table I. Characteristics of MgO Used\*

A.C.S. reagent-grade heavy powder	
Insoluble in HCl (%)	0.012
Soluble in H <sub>2</sub> O (%)	0.37
Ignition loss (%)	0.83
Ammonium hydroxide precipitate (%)	0.006
Chloride (Cl) (%)	0.003
Nitrate (NO <sub>3</sub> ) (%)	0.005
Sulfate and sulfite (as SO <sub>4</sub> ) (%)	0.002
Barium (Ba) (%)	0.005
Calcium (Ca) (%)	0.050
Heavy metals (as Pb) (%)	0.002
Iron (Fe) (%)	0.003
(MgO analysis supplied by manufacturer)	
Particle size ( $\mu$ )	<1
Specific surface area (m. <sup>2</sup> /gm.)†	16

\* MgO obtained from the Fisher Scientific Company, Pittsburgh, Pa. (Catalog No. M-51).

† Determined by the Morton Chemical Company, Chicago, Ill.

## III. Results and Discussion

The results of the controlled-atmosphere tests are presented in Table II. To obtain the best understanding of the delayed fracture process it seems desirable, following a brief summary of these results, to discuss the details of the experiments concurrently with the findings of other investigators. From Table II it is noted that cracking occurred in the following specimens (the experiments on which these statements are based are indicated in parentheses):

(1) Specimens exposed immediately to an unlimited amount of air unless the magnesium oxide powder had previously been exposed to air for extended periods of time before pressing (1A and 2A).

(2) Specimens exposed to successive amounts of fresh air when the total volume of the air was equal to a minimum of 15,000 ml. per specimen, about 2000 ml. per gm. (7A).

(3) Specimens exposed to certain mixtures of water vapor and CO<sub>2</sub> (12A).

(4) Specimens exposed to unlimited amounts of air, preceded by exposure to water vapor for about 2 weeks (14B).

(5) Specimens exposed to unlimited amounts of air preceded by storage in vacuum or in limited amounts of air for about 1 week (3B and 5B).

Cracking did not occur in the following specimens:

(1) Specimens exposed to vacuum or to limited amounts of air (3A, 4A, 5A, and 6A).

(2) Specimens exposed to air, preceded by storage in vacuum or in limited amounts of air for relatively long periods (4B and 6B).

(3) Specimens exposed to air at 110°C. (8A).

(4) Specimens exposed to unlimited amounts of air preceded by exposure to air at 110°C. (8B).

(5) Specimens exposed to dry CO<sub>2</sub>-free air (10A).

(6) Specimens exposed to CO<sub>2</sub> alone or to CO<sub>2</sub> with only minor amounts of water (11A).

(7) Specimens exposed to water vapor alone or to water vapor with only minor amounts of CO<sub>2</sub> (13A and 14A).

(8) Specimens exposed to unlimited amounts of air preceded by exposure to CO<sub>2</sub> (11B).

(9) Specimens exposed to unlimited amounts of air preceded by annealing in argon at 1250°C. (9B).

It also was noted that no cracking occurred in specimens which were pressed at only 2000 lb. per sq. in. and in specimens compacted from MgO powder prepared from MgCO<sub>3</sub>. (Presumably, the latter specimens retained enough CO<sub>2</sub> to prevent cracking.) The foregoing summary of the data suggests that the delayed fracture of the compacts is associated with the adsorption of both water and CO<sub>2</sub> and with critical residual stresses caused by the hydrostatic pressing.

Table II. Experimental Results

Ex- peri- ment No.	No. of speci- mens	First condition (A)*		Second condition (B)*	
		Specimen environment after pressing	Approximate time required for cracking	Environment	Approximate time required for cracking
1	10	Air	1½, † 1½, † 3, 3, 3, 3, 4, 4, 12, 18 hr.		
2	2	Air‡; 3 weeks	No cracks		
3	2	Limited amount of air (50 ml. per specimen); 1 week	No cracks	Air	15, 15 hr.
4	4	Limited amount of air (50 ml. per specimen); greater than 1 week	No cracks	Air; 3 weeks	No cracks
5	3	Vacuum; less than 2 weeks	No cracks	Air	2, 2, 7 hr.
6	5	Vacuum; greater than 2 weeks	No cracks	Air	No cracks
7	4	Successive 250 ml. portions of air per specimen (about 20-min. exposure to each portion)	48, 59, 59, 68th portion (about 20 hr.)		
8	2	110°C.; air; 1 week	No cracks	Air; 3 weeks	No cracks
9	8	Flowing argon; 1250°C.; 10 hr.	No cracks	Air; 3 weeks	No cracks
10	2	Unlimited amount of air dried by soda lime and Drierite§	128, 176 hr.		
11	4	250 ml. of 1 atm. CO <sub>2</sub> per specimen (both wet and dry); 2 weeks	No cracks	Air; 3 weeks	No cracks
12	2	Unlimited amount of sat. H <sub>2</sub> O vapor plus 250 ml. of 30 mm. CO <sub>2</sub> per specimen	45, 51 hr.		
13	2	Unlimited amount of sat. H <sub>2</sub> O vapor plus 50 ml. of 1 mm. CO <sub>2</sub> per specimen; 3 weeks	480 hr.; no cracks in one	Air	No cracks
14	4	Unlimited amount of sat. H <sub>2</sub> O vapor, CO <sub>2</sub> -free; 2 weeks	75 hr.; no cracks in three	Air	15, 185, 185 hr.

\* Unless otherwise specified, the environments were at room temperature.

† Powder dried in vacuum at 540°C. for 2½ days before used to prepare specimens.

‡ Powder exposed to air for 2 weeks before used to prepare specimens.

§ Because of the finite life of the drying agents and possible channeling in them, the air probably became wet by the time cracking occurred.

Table III. Chemical Analyses of Weight Gain\*

	Total increase in weight (%)	CO <sub>2</sub> (%)	Increase in CO <sub>2</sub> (%)	CO <sub>2</sub> to be adsorbed for monolayer† (%)	Increase in H <sub>2</sub> O (%)	H <sub>2</sub> O to be adsorbed for monolayer† (%)
Specimen not exposed		0.448				
Specimens exposed to air for 5 hr.	0.409	0.598	0.150	1.32	0.259	0.54
	0.417	0.599	0.151	1.32	0.266	0.54
	0.413	0.453	0.005	1.32	0.408	0.54
Specimen not exposed		0.52				
Specimens exposed to air for 3 weeks	2.78	1.90	1.38	1.32	1.40	0.54
	2.80	1.93	1.41	1.32	1.39	0.54
	2.81	1.84	1.32	1.32	1.49	0.54

\* The analysis of other specimens not presented here shows that the percentage of CO<sub>2</sub> is uniform throughout the specimen and corresponds to the amount picked up by uncompacted powder. Furthermore, the total percentage increase in weight is the same for compacts as for uncompacted powder.

† The calculations for the amount of CO<sub>2</sub> or H<sub>2</sub>O needed to form a monolayer are based on reaction with each surface site. The number of these sites was calculated from the surface area and dimensions of the unit cell in MgO. In other words,

$$\% \text{ CO}_2 = \frac{(M_{\text{CO}_2})(A)(S)(100)}{(N)(L)^2}$$

$M_{\text{CO}_2}$  = molecular weight of CO<sub>2</sub>.

$A$  = 2 = number of exposed surface anions per unit cell.

$S$  = specific surface area (sq. cm. per gm.) as determined by Brunauer-Emmett-Teller method.

$N$  = Avogadro's number.

$L$  = lattice parameter of MgO.

The value for water was calculated similarly.

Either water vapor or CO<sub>2</sub> alone is not sufficient to produce cracking. This interdependence can be more easily understood by referring to Bischoff's work, which showed that the adsorption of CO<sub>2</sub> on MgO was affected by the amount of water vapor which had previously been adsorbed.<sup>6</sup> Rieder and Schmidt extended these results and showed that a stoichiometrically defined compound was not produced.<sup>7</sup>

The present study shows that the amounts of water and CO<sub>2</sub> were adsorbed uniformly throughout the compacts and corresponded roughly to monomolecular layers on the surfaces of all the crystallites in the compacts (see Table III). This

point is given further confirmation in the work of Walker and Zettlemoyer, who found that the adsorption of CO<sub>2</sub> on pow-

<sup>6</sup> F. Bischoff, "Zur Frage der Rückreaktionen bei der thermischen Zersetzung von Kalkstein, Magnesit, und Dolomit" (Reverse Reaction in Thermal Decomposition of Limestone, Magnesite, and Dolomite), *Monatsh. Chem.*, **81**, 606-607 (1950).

<sup>7</sup> K. Rieder and H. Schmidt, "Vom Gleichgewicht MgO-H<sub>2</sub>O-CO<sub>2</sub>" (The Equilibrium MgO-H<sub>2</sub>O-CO<sub>2</sub>), *Berg- u. hütten-männ. Monatsh. montan. Hochschule Leoben*, **87**, 11-13 (1939).



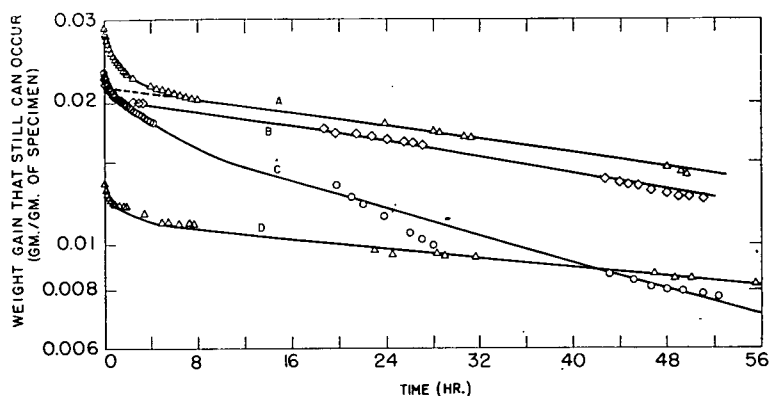


Fig. 2. First-order plot of weight-gain data. (A) Specimen No. 4, in humidified balance case, preceded by storage in an evacuated container for 5 weeks; (B) specimen No. 2, in humidified balance case; (C) specimen No. 3, in humidified balance case, preceded by storage in rubber-stoppered 60-ml. glass bottle (where specimen gained 0.0070 gm.) for 3 weeks; and (D) specimen No. 1, in balance case.

dered MgO amounted to monolayer coverage.<sup>8</sup> The present experiments involving successive fillings of a flask containing a specimen with air of normal humidity indicated that a substantial portion of a monolayer of water was necessary for the cracking of the specimens. The average number of 58 fillings required indicated that 0.11 gm. of water (50% humidity assumed) could have been adsorbed before cracking, if all the admitted water was adsorbed. This corresponded to 0.013 gm. of water per gram of specimen, compared with 0.005 gm. of water per gram of specimen necessary for a monolayer of water.

Additional information can be obtained from the consideration of the gain in weight of the specimens before cracking. In addition to considering such weight-gain data in terms of adsorption kinetics, one may interpret the data in terms of diffusion theory, since diffusion of water vapor and CO<sub>2</sub> through the open pores of the solid compact must occur before adsorption can take place on the surfaces of all the crystallites. If the partial pressures of water and CO<sub>2</sub> in the atmosphere were considered to be constant, the adsorption process would be pseudo first order with respect to adsorption sites, the rate constant being dependent on the partial pressure of water and/or CO<sub>2</sub>.

The weight changes of four specimens were determined as a function of time as mentioned in Section II. In about 400 hours the specimens reached a constant weight,  $W_{\infty}$ . If  $W_t$  is the weight of the specimen at time  $t$ , then  $W_{\infty} - W_t$  is the weight increase that still can occur. If a plot of  $\log(W_{\infty} - W_t)$  against  $t$  is linear, the data fit first-order kinetics. Except for a brief initial period the weight-gain data did indeed fit first-order kinetics as seen in Fig. 2. For one specimen the linear section was extrapolated to zero time, and the differences between the extrapolation and the original curve were obtained. These have been plotted in Fig. 3. This plot seems to indicate another first-order reaction. It is of interest to note that Jagitsch's data for the pickup of water by uncompact magnesium oxide also obeys first-order kinetics except for an initial rapid pickup.<sup>9</sup> Jagitsch claims zero-order kinetics (constant rate) for the first portion of his curve, but his initial

rate can be fitted just as well by first-order kinetics. Unfortunately, the extent of removal of CO<sub>2</sub> from his air stream is not indicated.

The half life\* for the first adsorption process in the present experiment (Fig. 3) was 1.3 hour. The half life for the second process (Fig. 2) was 73 hours. Since the adsorption of water was the more rapid process (Table III), it corresponded to the 1.3-hour half life whereas the adsorption of CO<sub>2</sub> corresponded to the 73-hour half life. This conclusion is in accord with the work of Burdese, who showed that the initial adsorption of water on MgO powders was complete after about 2 hours.<sup>10</sup> It is suggested, then, that fracture which normally developed about 3 hours after exposure to air occurred after the surfaces of the crystallites were largely covered with a water layer and only smaller amounts of adsorbed CO<sub>2</sub>.

Since both processes can be fitted by first-order kinetics, the adsorption processes themselves would seem to be the rate-controlling steps. The calculated half lives are reasonable for chemisorptions. The actual form of the chemisorbed layer could be one of several basic carbonates. (The most likely of these would seem to be hydromagnesite  $\text{Mg}_4(\text{OH})_2(\text{CO}_3)_3$  -

\* The half life is the time required to reduce the concentration of sites which will react to half their initial value.

<sup>10</sup> Aurelio Burdese, "Adsorbimento di vapor d'acqua su ossido di magnesio" (Adsorption of Water Vapor by Magnesium Oxide), *Atti accad. sci. Torino, Classe sci. fis., mat. e nat.*, **86**, 107-12 (1951-1952).

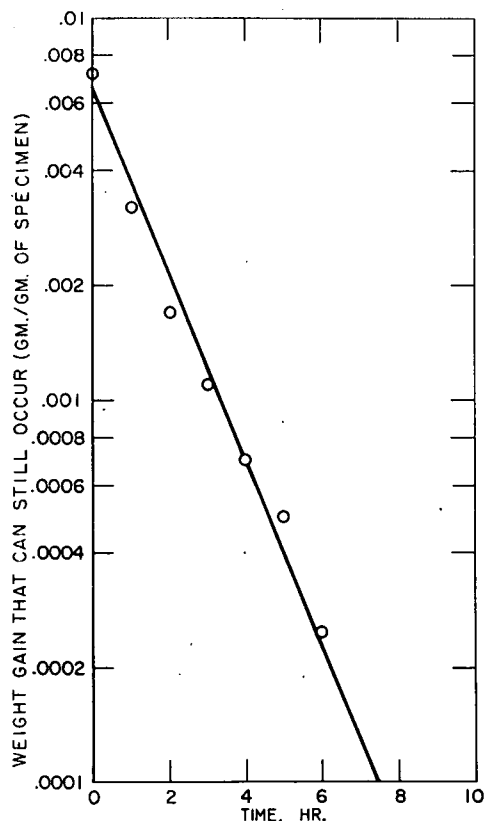


Fig. 3. First-order plot for initial reaction (specimen No. 4).

<sup>8</sup> W. C. Walker and A. C. Zettlemoyer, "Active Magnesia: V, Adsorption in Preferred Positions," *J. Phys. Chem.*, **57**, 182-86 (1953).

<sup>9</sup> Robert Jagitsch, "Untersuchung am System MgO-Wasser" (Investigation of the System MgO-Water), *Z. physik. Chem.*, **A181** [3] 215-20 (1937); *Ceram. Abstr.*, **17** [11] 347 (1938).

3H<sub>2</sub>O) or artinite (Mg<sub>2</sub>(CO<sub>3</sub>)(OH)<sub>2</sub>·3H<sub>2</sub>O), both of which have been observed to form during the rapid weathering of magnesium oxide rocks.<sup>11)</sup>

As mentioned earlier it was also reasonable to consider the data in terms of general diffusion theory. It therefore was of interest to calculate the rate of diffusion through the specimens. For short values of time, the appropriate equation for diffusion into a cylinder of radius,  $a$ , is<sup>12)</sup>

$$\frac{M_t}{M_\infty} = \frac{2DtL}{a^2} - \frac{8L^2}{2\pi^{1/2}} \left(\frac{Dt}{a^2}\right)^{1/2} - L^2 \left(\frac{Dt}{a^2}\right)^2 \left(\frac{1}{2} - L\right) \dots$$

$M_t$  = amount of diffusion species which has entered cylinder by time  $t$ .

$M_\infty$  =  $M_t$  at infinite time.

$D$  = diffusion coefficient.

$L$  =  $a\alpha/D$ .

$\alpha$  = proportionality constant in diffusion equation.

This equation is quite general for diffusion into a cylinder regardless of the type of diffusion occurring. In the present case, porosity and pore structure entered the equation by affecting the value of the diffusion coefficient,  $D$ . From this equation, one obtains

$$\frac{d^2M_t}{dt^2} = -\frac{2M_\infty L^2}{\pi^{1/2}} \left(\frac{D}{a^2}\right)^{1/2} (t)^{-1/2} - (L^2) \left(\frac{1}{2} - L\right) \left(\frac{D}{a^2}\right)^2 (2M_\infty)$$

A plot of  $d^2M_t/dt^2$ , obtained graphically from the experimental data, versus  $t^{-1/2}$  is presented in Fig. 4. By the simultaneous use of the slope and intercept of this curve, a diffusion coefficient of  $1.9 \times 10^{-4}$  sq. cm. per second was obtained for specimen No. 4. From similar plots for the other weighed specimens, the following diffusion coefficients were obtained:

Specimen No. 1	$D = 3.2 \times 10^{-4}$ sq. cm. per second
Specimen No. 2	$D = 2.0 \times 10^{-4}$ sq. cm. per second
Specimen No. 3	$D = 2.5 \times 10^{-4}$ sq. cm. per second

These values are of proper magnitude for gas diffusion coefficients through the open pores of the compact. (Values of this order of magnitude have been obtained for diffusion of gases through porous compacts by Dacey and Fendley<sup>13)</sup> and by Hoogschagen.<sup>14)</sup> It is obvious from the experimental data that one cannot state whether the rate of weight gain during the first hour was controlled by diffusion or by adsorption. However, either process is consistent with the general concept of the formation of a surface layer of some basic magnesium carbonate.

One can now propose a mechanism to explain the delayed cracking. The hydrostatic pressing of the powder causes stresses which are not relieved upon the release of the pressure. The mere presence of these residual stresses is not a condition sufficient to initiate cracking; it is necessary to modify the mechanical equilibrium through some localized chemical or physical change of the compact. The experiments suggest that the chemical attack on microscopic regions of the surfaces of the individual crystallites, perhaps at highly stressed contact sites, causes rapid modification of physical properties (hardness and density). This results in a catastrophic stress redistribution and leads to cracking.

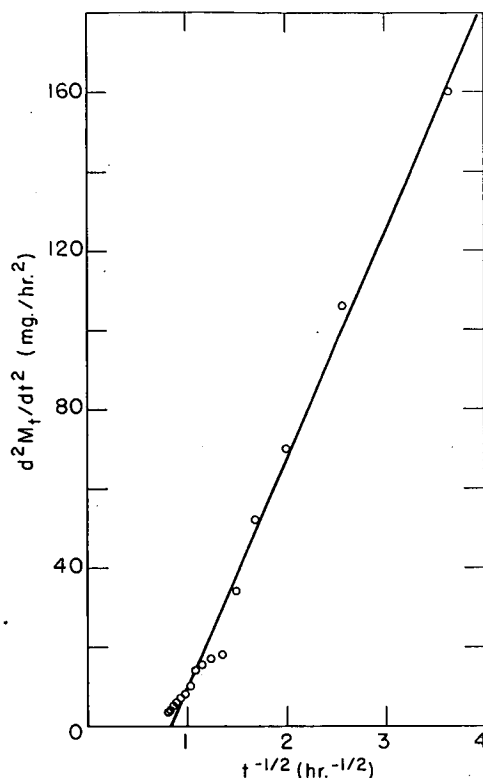


Fig. 4. Evaluation of weight-gain data in terms of diffusion theory (specimen No. 4).

The experiments indicate that the occurrence of a catastrophic stress redistribution is very specific as to the reaction which occurs in the system MgO-H<sub>2</sub>O-CO<sub>2</sub>. Such a dependence on the reaction may be due either to the speed of the chemical reaction or to the nature of the reaction product. Experimentally, it has been found that when CO<sub>2</sub> is chemisorbed at the high-energy sites, no cracking occurs. When, on the other hand, water vapor is adsorbed first, no cracking results until the softer, less dense basic carbonates are formed by subsequent reaction with CO<sub>2</sub>.

If the cracking experiments are now reviewed, it is noted that the results from all but one of the 54 specimens tested support the proposed mechanism. Moreover, certain unexpected results from experiments 2A, 4B, and 6B are clarified. No cracking occurred in specimens pressed from powders which were originally exposed to CO<sub>2</sub> and water. This was to be expected since in this case the compacts were not initially MgO but some form of the basic carbonate which would not have the ability for further reaction to initiate cracking. Some of the pressing characteristics may also be different. It also has been found that cracking does not occur in compacts of MgO prepared from MgCO<sub>3</sub>. In experiments 9A and 9B, it was observed that the residual stresses could be reduced below the critical value by annealing procedures. It is not too surprising, therefore, in experiments 4B and 6B, that slow annealing of stresses should occur at room temperatures when the specimens were protected from large amounts of CO<sub>2</sub> and water for times longer than those required for annealing.

When all three of the factors, residual stresses and adequate amounts of water and CO<sub>2</sub>, were present, cracking occurred. To prevent cracking, at least one factor must be absent. It is apparent from the experiments that cracking can be prevented by any of several methods: storage for about 2 weeks *in vacuo* or in an atmosphere where the amount of water and CO<sub>2</sub> is small, storage in a CO<sub>2</sub> atmosphere for shorter periods of time, or annealing of the pressed compacts.

<sup>11</sup> Charles Palache, Harry Berman, and Clifford Frondel (editors), Dana's System of Mineralogy, Vol. I, 7th ed., 1944. 834 pp. Vol. II, 7th ed., 1951. 1124 pp. John Wiley & Sons, Inc., New York; *Ceram. Abstr.*, 1953, April, p. 74b.

<sup>12</sup> J. Crank, Mathematics of Diffusion, p. 73. Clarendon Press, Oxford, 1956. 347 pp.

<sup>13</sup> Structure and Properties of Porous Materials—Proceedings of the Tenth Symposium of the Colston Research Society held at the University of Bristol, 1958, p. 148. D. H. Everett and F. S. Stone (editors). Butterworth Scientific Publications, London; Academic Press, Inc., New York, 1958. 389 pp.; *Ceram. Abstr.*, 1960, June, p. 152c.

<sup>14</sup> Jan Hoogschagen, "Diffusion in Porous Catalysts and Adsorbents," *Ind. Eng. Chem.*, 47 [5] 906-13 (1955).